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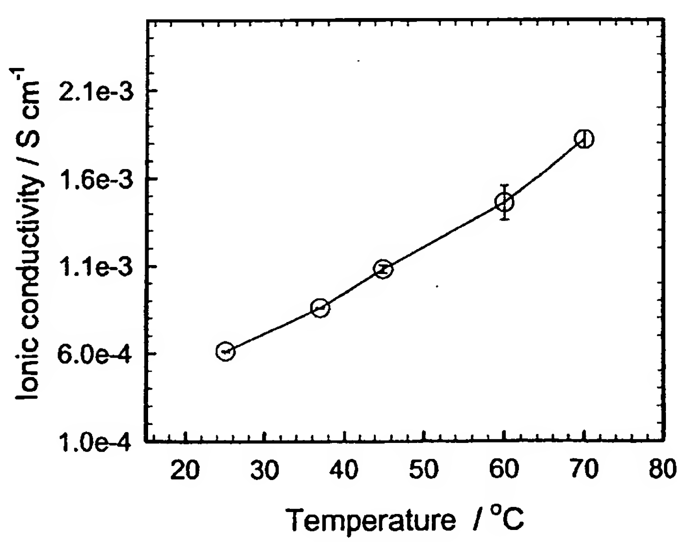
(54) Title: NONAQUEOUS LIQUID ELECTROLYTE



(57) Abstract: Disclosed is a nonaqueous and nonvolatile liquid type polymeric electrolyte comprising poly(siloxane-g-ethylene oxide). This electrolyte provides significant safety and stability. The present invention solves the problems of volatility, flammability and chemical reactivity of lithium ion type electrolytes. The disclosed electrolyte exhibits excellent stability, conductivity and low impedance characteristics. The electrolyte comprises a new class of structural siloxane polymers with one or more poly(ethylene oxide) side chains. The inorganic siloxanes comprising the main backbone of the copolymers are thermally very stable and resistant to decomposition by heat. Because the main chain of the disclosed class of electrolytes is an Si-O linkage, initiation of the combustion cycle is inhibited or prevented.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Nonaqueous Liquid Electrolyte

GOVERNMENT LICENSE RIGHTS

This invention was made with United States Government support under NIST ATP Award No. 70NANB043022 awarded by the National Institute of Standards and Technology (NIST). The United States Government has certain rights in this invention pursuant to NIST ATP Award No. 70NANB043022 and pursuant to Contract No. W-31-109-ENG-38 between the United States Government and the University of Chicago representing Argonne National Laboratory.

TECHNICAL FIELD

The present invention relates to electrochemical storage devices containing a nonaqueous electrolyte with high ionic conductivity and nonvolatile characteristics. More particularly, the present invention relates to liquid type polymeric electrolytes that are superior in ionic conductivity, thermal stability, and safety to most of those currently being used in lithium-ion cells today.

BACKGROUND

The demand for lithium secondary batteries to meet high power and high-energy system applications has resulted in substantial research and development activities to improve their safety, as well as performance. As the world becomes increasingly dependent on portable electronic devices, and looks toward increased use of electrochemical storage devices for vehicles, power distribution load leveling and the like, it is increasingly important that the safety of such devices be paramount, especially as these devices are being used in such environments as airliners and space vehicles. The effort to date has included research in flame-retardants, solid polymer electrolytes and new electrolyte concepts with improved thermostability. Thus, the development of highly conductive electrolytes, free of any problems associated with volatile and combustible solvents, is of paramount importance. Electrolytes based on polymeric structures have basically better heat and chemical resistance than conventional organic carbonate-based electrolytes and can thus reduce many chemical side reactions occurring in lithium secondary batteries. Although, polymeric based electrolytes have many advantages over carbonate solvent based electrolytes, their application in lithium secondary batteries has been limited due to their low ionic conductivity, usually below 10^{-5} S/cm at room temperature.

To solve this problem, new electrolyte concepts are needed. The new electrolytes should be nonvolatile materials that have excellent electrochemical properties, such as high

ionic conductivity of over 10^{-4} S/cm at room temperature and wide electrochemical stability windows of over 4.5 V (based on lithium metal).

Accordingly, the present inventors have developed a new type of ionically conductive electrolyte based on various polymeric structures, especially having a poly(siloxane-*g*-ethylene oxide) composition which overcomes the above mentioned problems of volatility, flammability and chemical reactivity inside of the lithium battery. The proposed liquid type poly(siloxane-*g*-ethylene oxide) materials also have an excellent electrochemical stability window and favorable room temperature ionic conductivity.

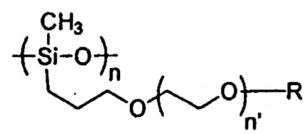
Carbonate solvents, such as ethylene carbonate and ethyl-methyl carbonate used for conventional lithium battery electrolytes can easily burn from low temperature sources of ignition and generate flame, carbon dioxide and H_2O during thermal degradation. This is a critical problem in high capacity battery applications like lithium batteries for electric vehicles (EV) and satellites. Polymeric materials, however, usually have a somewhat different combustion mechanism than the carbonates. The initial stage of a fire occurs when a heat source decomposes the polymeric materials to flammable volatile products. Thus, for continuous burning to occur, (a) the application of heat must be sufficient to decompose the polymer, (b) the temperature must be sufficient to ignite the products of decomposition, and (c) the amount of heat transferred from the flame back to the polymer must be sufficient to maintain the cycle. In general, polymeric materials are more thermally stable than low molecular weight chemicals like the organic carbonates because they are not volatile and are vaporized at much higher temperatures.

The present inventors have carefully considered the combustion mechanisms of polymeric materials and concluded that to stop the propagation of the burning cycle one needed to develop new polymer materials that are thermally more stable and capable of dissolving the lithium salts to prepare electrolytes for electrochemical devices such as lithium batteries and/or capacitors. The present inventors have developed new structural siloxane polymers with one or more poly(ethylene oxide) side chains. Siloxanes are very thermally stable and are decomposed by heat with difficulty. Only a few flammable by-products are formed during the thermal decomposition of such polymers because their main chain is a Si-O linkage. Thus, its presence in the proposed polymers will delay the initiation of the combustion cycle.

Due to the merits of siloxane-poly(ethylene oxide) graft copolymers, substantial research has been done. *See*, for example, U.S. Pat. No. 5,112,512 to Nakamura and U.S. Pat. No. 6,124,062 to Horie et al. also describing siloxane-poly(ethylene oxide) graft copolymers

(as a polymeric electrolyte material. The '512 patent discloses a crosslinked polymer electrolyte based on the graft copolymers, but its ionic conductivity is too low for room temperature applications. The '062 patent discloses direct use of siloxane-poly(ethylene oxide) grafted copolymers as a liquid for a lithium battery electrolyte with ionic conductivity of around 10^{-4} S/cm at ca. 25°C. (*See* General Formula I). The conductivity of the material disclosed in the '062 patent is disadvantageously low. In addition, the cost of such material is relatively high. The present inventors have discovered a much improved material with higher conductivity and lower cost.

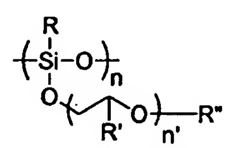
General formula (I) (as disclosed in the '062 patent):



wherein R is alkyl group.

The present inventors developed an improved liquid state siloxane polymer with one or more poly(ethylene oxide) side chains to ensure thermal stability and electrochemical properties. Poly(ethylene oxides) (PEO) in poly(siloxane-*g*-ethylene oxide) materials of this invention (*see* general formula II) are directly bonded to a Si atom. Poly(siloxane-*g*-ethylene oxide) materials of the present invention are easily synthesized through a simple dehydrocoupling reaction with simple metal carbonate based catalysts and the cost for synthesis of poly(siloxane-*g*-ethylene oxide) of this invention is much lower than the cost of synthesis of general formula (I) with a propylene spacer between siloxane and PEO. The present inventors also control the viscosity of the materials to get high ionic conductivities of around 10^{-3} S/cm at room temperature.

General formula (II):



where R and R" are alkyl groups and R' is hydrogen or alkyl group.

As compared to the material disclosed in the '062 patent, ionic conductivity is improved by changing the chemical structure of siloxane, that is, directly grafting ethylene oxide onto Si atom without any alkyl carbon spacer between them. Changing the structure in this way increases hydrophilicity and solubility, leading to higher conductivity.

OBJECTIVES

A primary objective of the present invention is to provide a safe liquid electrolyte for use in lithium ion type cells and allied devices such as super capacitors and hybrid devices.

Specifically, a primary objective is to reduce or eliminate problems associated with volatility, flammability and chemical reactivity of liquid electrolytes.

A further objective of the invention is to provide a lithium-based secondary battery, capacitor or hybrid device with enhanced safety and excellent performance characteristics by use of the present polymeric electrolyte.

SUMMARY

Accordingly, the present invention relates to lithium-based secondary batteries with a nonaqueous and nonvolatile polymeric electrolyte with high room temperature ionic conductivity with enhanced safety.

The invention also relates to nonaqueous and nonvolatile polymeric electrolytes processing controlled viscosity for the high-energy lithium secondary battery applications, especially for electric vehicles and satellite applications.

To fulfill the above objectives, the nonaqueous and nonvolatile polymeric electrolyte solutions in the present invention is prepared by using the compositions which comprise poly(siloxane-*g*-ethylene oxide) in a liquid state with proper viscosity and a dissolved lithium salt.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a trace of measured ionic conductivity vs. temperature for a cell made according to the present invention.

Figure 2a and 2b are traces of cyclic voltammetry measurements to determine electrochemical stability of samples made according to the present invention.

Figure 3 is a trace of measured ionic conductivity showing the effect of doping level, on the ionic conductivity of poly(siloxane-g-3 ethylene oxide) electrolyte at two different temperatures.

Figure 4 is a trace of measured ionic conductivity of poly(siloxane-*g*-3 ethylene oxide) electrolyte with $LiPF_6$ in place of LiTFSI at a doping level of 32:1.

FIGURE 5a is a data trace from accelerating rate calorimetry (ARC) tests of the electrolyte of the present invention.

FIGURE 5b is a comparative data trace from ARC tests of liquid electrolyte $LiPF_6$ in a mixture of ethylene carbonate and ethyl methyl carbonate.

Figure 6 is a graph of the results of comparative flame tests based on Underwriters Laboratories UL94 standard.

DETAILED DESCRIPTION

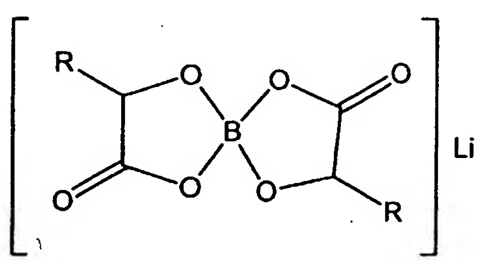
The electrolyte solution of the present invention comprises siloxane polymers with one or more poly(ethylene oxide) as a side chain (see general formula II above). The inorganic siloxane main body ensures flame-retardancy and chemical stability, and poly(ethylene oxide) side chains give ionic conducting phases. A poly(ethylene oxide) group is directly grafted to silicon atoms in the siloxane polymer. The poly(siloxane-g-ethylene oxides) of the present invention are easily synthesized through simple dehydrogenation reactions to avoid problems that come from the use of metal catalysts such as platinum.

The poly(siloxane-*g*-ethylene oxide) easily dissolves lithium salt and has enough flexibility to transport lithium ions. Through the viscosity control of the poly(siloxane-*g*-ethylene oxide), the polymeric electrolyte solution provides excellent ionic conductivity of around 10^{-3} S/cm at room temperature.

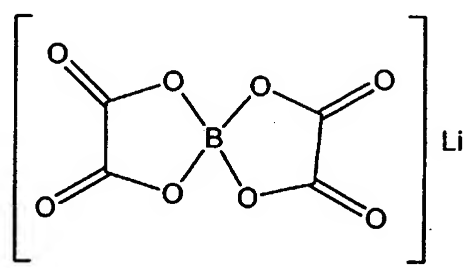
The lithium salt to be used in the present invention is not particularly limited, as long as it serves as an electrolyte for a lithium secondary battery. Examples of specific lithium salts include, but are not limited to, $LiClO_4$, $LiBF_4$, $LiAsF_6$, $LiPF_6$, $LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, $Li(CF_3SO_2)_3C$, $LiN(SO_2C_2F_5)_2$, lithium alkyl fluorophosphates, and mixtures thereof.

Further examples (without the intent to limit the scope of the invention) found to be beneficial are lithium bis(chelato)borates having from five to seven-membered rings as follows:

Five-membered rings

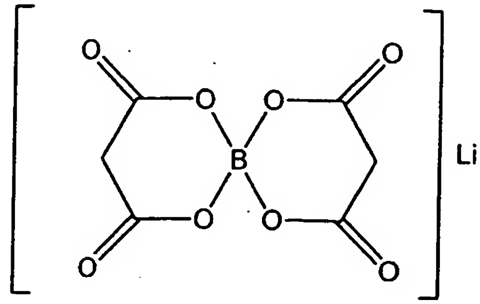


Where R is H or an alkyl group.

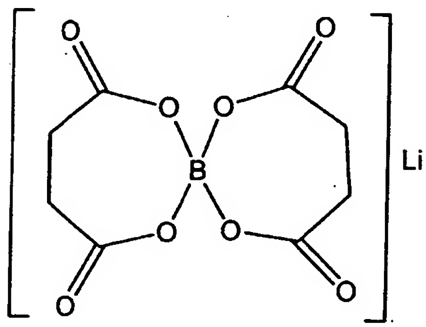


lithium bis(oxalato)borate (LiBOB)

Six-membered ring



Seven-membered ring



The oxygen versus Li ratio (doping level) is preferably 5:1 to 50:1. If the doping level is greater than 50:1, the ionic conductivity of the resulting polymeric electrolyte is undesirably decreased because of the number of ions present in the solid polymer electrolyte. If the doping level is smaller than 5:1, the lithium salt is not sufficiently dissociated in the resulting polymeric electrolyte and the association of lithium ion reduces the ionic conductivity. Preferably, the average molecular weight of the poly(siloxane-*g*-ethylene oxide) should not exceed 20,000 g/mol. This corresponds to $3<n\leq 250$ in General Formula (II). The dynamic viscosity of the poly(siloxane-*g*-ethylene oxide) is best in the range of 200 cPs, should preferably not exceed 1,000 cPs to 2,000 cPs, and should never exceed 10,000 cPs.

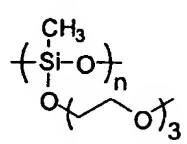
The present invention covers both polymeric electrolytes as well as the lithium secondary batteries that use them in the same way that the carbonate based electrolytes are applied in the state-of-the-art Li-ion batteries today. A lithium secondary battery with the polymeric electrolyte solution of this invention as a conducting medium can be fabricated by injecting the polymeric electrolyte solution into a spiral wound cell or prismatic type cell. It

can be also coated onto the surface of electrodes and assembled with a porous separator to fabricate single or multi-stacked cells that are packaged with plastic pouches. Similarly, the electrolyte of the present invention may be used in ultra capacitors (also known as super capacitors) and hybrid devices incorporating aspects of batteries and capacitors.

In situ tests: Type 2032 button cells were assembled for the evaluation of cell performance with a MAG-10 anode, and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ as a cathode. Celgard® 2500 (microporous polypropylene membrane, available from CELGARD Inc.) was used as a separator. These cells contained MAG-10 graphite, with 8 wt% PVDF binder/ poly(siloxane-*g*-3 ethylene oxide), doping level of 32:1 with LiTFSI, electrolyte/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, 8 wt% PVDF, 4 wt% SFG-6 graphite, and 4 wt% carbon black. The effective cell area was 1.6 cm^2. Charge and discharge rate were C/10. There was no degradation peak caused by the metal oxide up to 4.1V and the specific charge capacity was over 140 mAh/g.

Figure 1 shows the effect of temperature on the ionic conductivity of poly(siloxane-*g*-3 ethylene oxide) electrolyte (see general formula III). Poly(siloxane-*g*-3 ethylene oxide) and $Li(CF_3SO_2)_2N$ were mixed with a doping level of 32:1. The ionic conductivity of the polymeric electrolytes at temperatures ranging from 25 to 70°C were measured from the AC impedance curves from type 2030 button cells assembled by injecting the polymeric electrolyte between two stainless steel discs with a glass filter (750 micron thick) to prevent short circuits. The measuring frequency range was from 1 MHz to 10 Hz.

General formula (III):



Poly(siloxane-*g*-3 ethylene oxide) electrolyte shows an excellent ionic conductivity of 8.6×10^{-4} S/cm at 37°C.

Figures 2a and 2b show the electrochemical stability of poly(siloxane-*g*-3 ethylene oxide) and poly(siloxane-*g*-7 ethylene oxide) (*see* general formula IV) electrolytes, respectively. Poly(siloxane-*g*- ethylene oxides) and $Li(CF_3SO_2)_2N$ were mixed with a doping level of 32:1. The electrochemical stability window of the polymer electrolytes were determined by cyclic voltammetry with type 2030 button cells assembled by sandwiching a glass filter containing the polymer electrolyte between a stainless steel disc as a working electrode and a lithium metal disc as a combined counter and reference electrode. These polymeric electrolytes were found to show excellent electrochemical stability windows over 0 to 4.5V(vs. Li) and only a minimal decomposition peak around 4.5V during the first anodic

sweep. In the case of poly(siloxane-g-7 ethylene oxide), which is more stable, the stability window reaches ca. 5.5 V.

General formula (IV)

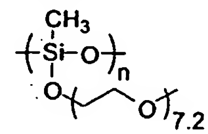


Figure 3 is a trace of measured ionic conductivity vs. doping level at two different temperatures (24° C and 60° C). These data show the effect of doping level, O vs. Li^+, on the ionic conductivity of poly(siloxane-g-3 ethylene oxide) electrolyte (see general formula III). A doping level of 32:1 is an optimum formulation regardless temperature. In the case of doping level of 15:1, there is an improvement of ionic conductivity at 60°C owing to the additional dissociation of lithium cluster formed at 24°C. A high concentration of lithium salt generally creates clusters at lower temperature, but can be dissociated a bit by increasing temperature.

Figure 4 shows the ionic conductivity of poly(siloxane-g- 3 ethylene oxide) electrolyte with $LiPF_6$ in place of LiTFSI at a doping level of 32:1. Even though $LiPF_6$ has smaller anion than LiTFSI, the ionic conductivity values are similar to that shown in Figure 1. This is due to the highly flexible structure of poly(siloxane-g- 3 ethylene oxide). The highly flexible structure of the siloxane electrolyte of this invention can overcome the lack of plasticizing effect by the anion part of lithium salt. Poly(siloxane-g- 3 ethylene oxide) has the additional advantage of increasing the variety of usable lithium salts over that of General formula (I) (as disclosed in the '062 patent), siloxane with alkyl carbon spacer between Si and polyethylene oxide. This comes from the fact that the rotation barrier of the Si-O bond is less than 0.2 kcal, but that of $Si-CH_3$ is 1.6 kcal (*see*, C.F. Rome, Hydrocarbon Asia, May/June (2001) 42-49).

Figure 5(a) shows thermal stability of poly(siloxane-*g*-3 ethylene oxide) electrolyte at a doping level of 32:1 with $LiPF_6$, using accelerating rate calorimetry ("ARC"). A heat-wait-search sequence was applied. Sample weight for the test was 500mg. Each sample was introduced in a 2¼" x ¼" diameter stainless steel bomb for the ARC test.

ARC is more sensitive test method than differential scanning calorimetry ("DSC"). In a heat-wait-search sequence, ARC will search an exothermic reaction for 30minutes at every 5°C change from the starting temperature. In DSC, a 5 or 10°C/min heating rate is usually used and the sample quantity is only about 2 to 5 μL. In the case of some chemicals, the exothermic peak by DSC comes later than ARC due to its much faster scan rate than ARC.

Although solid $LiPF_6$ itself decomposes to PF_5 and LiF at about 250°C, as measured by the DSC method, (*see*, N. Katayama et al., J. Power Sources, 2001, in press at time of application) and PF_5 reacts with solvents for further thermal decomposition, poly(siloxane-*g*-3 ethylene oxide) electrolyte has an exothermic peak above 300°C. This means that poly(siloxane-*g*-3 ethylene oxide) has excellent chemical stability even at an elevated temperature.

Figure 5b shows comparative data from an ARC test of a widely used liquid electrolyte, 1.2M $LiPF_6$ in ethylene carbonate (EC):ethyl methyl carbonate (EMC) (3:7 weight ratio). This sample was tested in the same way as in Figure 5a. Its exothermic peak is detected before 200°C (approximately. 220°C of onset temperature by DSC; *see*, N. Katayama et al., J. Power Sources, 2001, in press at time of application). It is thus found that the siloxane main backbone of poly(siloxane-*g*-ethylene oxide) significantly enhances the thermal stability of the electrolyte.

Figure 6 is a graph of the results of a flame tests (propagation rate) based on Underwriters Laboratories UL94 standard. Flammability of poly(siloxane-*g*-3 ethylene oxide) electrolyte, doping level of 32:1 with $LiPF_6$, was investigated using modified UL-94HB Horizontal Burning Test. Detail compositions of the test samples are listed in Table 1.

	Composition	Other
EC:DEC	1M $LiPF_6$ in EC:DEC (1:1 by wt)	
EC:EMC	1.2M $LiPF_6$ in EC:EMC (3:7 by wt)	
EC:PC:EMC	1M $LiPF_6$ in EC:PC:EMC (3:3:4 by wt)	
4PEGDME	Poly(ethylene glycol) dimethyl ether + $LiPF_6$	4 ethylene oxide $O/Li^+ = 20:1$
PMHS3C	Poly(siloxane-g-3 ethylene oxide) + $LiPF_6$	$O/Li^+ = 32:1$

Table 1

UL intends this standard to serve as a preliminary indication of the acceptability of materials for use as part of electronic goods, lithium batteries, etc. with respect to flammability.

The modified UL-94HB test uses a ¼" x 5.5" silanized glass wool wick specimen soaked with the electrolyte samples held at one end in a horizontal position with marks at 1.00" and 4.94" from the free end. The specimen contains 5g of electrolyte. A flame is applied to the free end for 30 seconds or until the flame front reaches the 1" mark. If

combustion continues the duration is timed between the 1.00" mark and the 4.94" mark. If combustion stops before the 4.94" mark, the time of combustion and the damaged length between the two marks are recorded. A set of five specimens is tested. If two specimens from the set of five fail to comply, then a second set of five are tested. All five of this second set must comply. Propagation rate of flame is given by the following equation:

Propagation Rate = Distance (cm) / Elapsed time (min)

Poly(siloxane-g-3 ethylene oxide) electrolyte shows outstanding flame resistance. Its propagation rate is significantly lower than conventional liquid electrolyte for lithium ion batteries and low molecular weight polyethylene oxide electrolyte. This is because the inorganic siloxane backbone naturally acts as a combustion inhibitor.

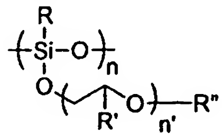
It should be apparent that the present invention solves the long-felt need to create safe, high energy electrochemical storage devices having liquid electrolytes. Such devices promise to have high energy rate capabilities as well as high energy density. Batteries containing the present electrolyte, especially large batteries such as those used in electric vehicles, would be inherently safer than those with more volatile, flammable and unstable electrolytes.

Having described the present invention, it should be apparent to the reader that many variations of the present invention are possible without departure from the scope of the present invention. The specific implementations disclosed above are by way of example and for the purposes of enabling persons skilled in the art to implement the invention only. Accordingly, the invention is not to be limited except by the appended claims and legal equivalents.

Claims

We claim:

1. A nonaqueous liquid type polymeric electrolyte comprising poly(siloxane-g-ethylene oxide) represented by general formula



, where R and R" are alkyl groups and R' is a hydrogen or alkyl group, and at least one dissolved alkali metal salt for electrochemical devices.

2. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the average molecular weight of the poly(siloxane-*g*-ethylene oxide) does not exceed 20,000 g/mol.

3. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the dynamic viscosity of the poly(siloxane-*g*-ethylene oxide) does not exceed 10,000 cPs.

4. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the dynamic viscosity of the poly(siloxane-*g*-ethylene oxide) does not exceed about 2,000 cPs.

5. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the dynamic viscosity of the poly(siloxane-*g*-ethylene oxide) does not exceed 200 cPs.

6. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the alkali metal salt is a lithium salt.

7. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein said dissolved a alkali metal salt comprises at least one quaternary ammonium salt having an anion selected from the following group: ClO_4^-, BF_4^-, AsF_6^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(CF_3SO_2)_3C^-$, $N(SO_2C_2F_5)_2)^-$, $PF_3(C_2F_5)_3^-$, $PF_3(CF_3)_3^-$, and $B(C_2O_4)_2^-$.

8. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the lithium salt comprises $LiClO_4$, $LiBF_4$, $LiAsF_6$, $LiPF_6$, $LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, $Li(CF_3SO_2)_3C$, $LiN(SO_2C_2F_5)_2$, $LiPF_3(C_2F_5)_3$, $LiPF_3(CF_3)_3$, $LiB(C_2O_4)_2$ or mixtures thereof.

9. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the lithium salt comprises lithium bis(chelato)borate having five to seven rings.

10. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein said electrolyte is non-volatile.

11. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the oxygen versus lithium ratio is 5:1 to 50:1.

12. The nonaqueous liquid type polymeric electrolyte of claim 1, further characterized by having an ionic conductivity of at least $6x10^{-4}$ S/cm at room temperature and at least $8.4x10^{-4}$ S/cm at 37° C.

13. The nonaqueous liquid type polymeric electrolyte of claim 1, further characterized by having a viscosity of not more than about 1,000 cPs.

14. An electrochemical device comprising the nonaqueous liquid type polymeric electrolyte of claim 1.

15. The electrochemical device of claim 14 wherein said dissolved a alkali metal salt comprises at least one quaternary ammonium salt having an anion selected from the following group: ClO_4^-, BF_4^-, AsF_6^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(CF_3SO_2)_3C^-$, $(C_2F_5SO_2)_2N^-$, $PF_3(C_2F_5)_3^-$, $PF_3(CF_3)_3^-$ and $B(C_2O_4)_2^-$.

16. The electrochemical device of claim 14 wherein said dissolved alkali metal salt comprises lithium bis(chelato)borate having five to seven membered rings.

17. The electrochemical device of claim 15 or 16 where said electrochemical device comprises a secondary battery.

18. The secondary battery of claim 17 further comprising a lithium metal oxide or lithium metal phosphate positive electrode, at least one porous separator, and at least one lithium-carbon, lithium-alloy, or lithium metal negative electrode.

19. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises at least one lithium salt.

20. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $LiCF_3SO_3$.

21. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $Li(CF_3SO_2)_2N$.

22. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $LiC(CF_3SO_2)_3$.

23. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $LiN(SO_2C_2F_5)_2$.

24. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $LiPF_6$.

25. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $LiAsF_6$.

26. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $LiBF_4$.

27. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $LiClO_4$.

28. The electrochemical device of claim 14 wherein said dissolved alkali metal salt includes at least one electrolyte salt from the following group: $LiClO_4$, $LiBF_4$, $LiAsF_6$, $LiPF_6$, $LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, $Li(CF_3SO_2)_3C$, $LiN(SO_2C_2F_5)_2$, $LiPF_3(C_2F_5)_3$, $LiPF_3(CF_3)_3$, $LiB(C_2O_4)_2$.

29. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $LiPF_3(C_2F_5)_3$.

30. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $LiPF_3(CF_3)_3$.

31. The secondary battery of claim 17 wherein said dissolved alkali metal salt comprises $LiB(C_2O_4)_2$.

32. The electrochemical device of claim 14 wherein said device is a capacitor.

33. The capacitor of claim 32 wherein said dissolved alkali metal salt comprises at least one quaternary ammonium salt having an anion selected from the following group: ClO_4^-, BF_4^-, AsF_6^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(CF_3SO_2)_3C^-$, $(C_2F_5SO_2)_2N^-$, $PF_3(C_2F_5)_3^-$, $PF_3(CF_3)_3^-$, and $B(C_2O_4)_2^-$.

34. A nonaqueous liquid type polymeric electrolyte having an ionic conductivity of at least $6x10^{-4}$ S/cm at 25° C.

35. A nonaqueous liquid type polymeric electrolyte having an ionic conductivity of at least $8.4x10^{-4}$ S/cm at 37° C.

36. The nonaqueous liquid type polymeric electrolyte of claim 34 further characterized by having ionic conductivity of at least $8.4x10^{-4}$ S/cm at 37°C.

37. A lithium secondary battery containing the nonaqueous liquid type polymeric electrolyte of claim 34.

38. A capacitor containing the nonaqueous liquid type polymeric electrolyte of claim 34.

39. A lithium secondary battery containing the nonaqueous liquid type polymeric electrolyte of claim 35.

40. A capacitor containing the nonaqueous liquid type polymeric electrolyte of claim 35.

41. The nonaqueous liquid type polymeric electrolyte of claim 34 wherein said electrolyte is nonvolatile.

42. The nonaqueous liquid type polymeric electrolyte of claim 35 wherein said electrolyte is nonvolatile.

43. The nonaqueous liquid type polymeric electrolyte of claim 34 wherein said electrolyte is electrochemically stable over 4.5 V.

44. The nonaqueous liquid type polymeric electrolyte of claim 35 wherein said electrolyte is electrochemically stable over 4.5 V.

45. The nonaqueous liquid type polymeric electrolyte of claim 36 wherein said electrolyte is nonvolatile.

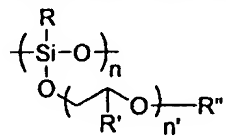
46. The nonaqueous liquid type polymeric electrolyte of claim 36 wherein said electrolyte is electrochemically stable over 4.5 V.

AMENDED CLAIMS

[received by the International Bureau on 25 june 2003 (25.06.03);
original claims1-46 replaced by amended claims 1-46 (4 pages)]

1. A nonaqueous liquid type polymeric electrolyte comprising:

poly(siloxane-g-ethylene oxide) represented by general formula



, where R and R" are alkyl groups and R' is a hydrogen or alkyl group; and

at least one dissolved salt for electrochemical devices.

2. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the average molecular weight of the poly(siloxane-g-ethylene oxide) does not exceed 20,000 g/mol.

3. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the dynamic viscosity of the poly(siloxane-g-ethylene oxide) does not exceed 10,000 cPs.

4. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the dynamic viscosity of the poly(siloxane-g-ethylene oxide) does not exceed about 2,000 cPs.

5. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the dynamic viscosity of the poly(siloxane-g-ethylene oxide) does not exceed 200 cPs.

6. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the salt is a lithium salt.

7. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein said dissolved salt comprises at least one quaternary ammonium salt having an anion selected from the group consisting of: ClO_4^-, BF_4^-, AsF_6^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(CF_3SO_2)_3C^-$, $(C_2F_5SO_2)_2N^-$, $PF_3(C_2F_5)_3^-$, $PF_3(CF_3)_3^-$, and $B(C_2O_4)_2^-$.

8. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the salt comprises $LiClO_4$, $LiBF_4$, $LiAsF_6$, $LiPF_6$, $LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, $LiC(CF_3SO_2)_3$, $LiN(SO_2C_2F_5)_2$, $LiPF_3(C_2F_5)_3$, $LiPF_3(CF_3)_3$, $LiB(C_2O_4)_2$, or mixtures thereof.

9. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the salt comprises lithium bis(chelato)borate having five to seven rings.

10. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein said electrolyte is nonvolatile.

11. The nonaqueous liquid type polymeric electrolyte of claim 1, wherein the oxygen versus lithium ratio is 5:1 to 50:1.

12. The nonaqueous liquid type polymeric electrolyte of claim 1, further characterized by having an ionic conductivity of at least 6×10^{-4} S/cm at room temperature and at least 8.4×10^{-4} S/cm at 37°C.

13. The nonaqueous liquid type polymeric electrolyte of claim 1, further characterized by having a viscosity of not more than about 1,000 cPs.

14. An electrochemical device comprising the nonaqueous liquid type polymeric electrolyte of claim 1.

15. The electrochemical device of claim 14 wherein said dissolved salt comprises at least one quaternary ammonium salt having an anion selected from the group consisting of: ClO_4^-, BF_4^-, AsF_6^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(CF_3SO_2)_3C^-$, $(C_2F_5SO_2)_2N^-$, $PF_3(C_2F_5)_3^-$, $PF_3(CF_3)_3^-$, and $B(C_2O_4)_2^-$.

16. The electrochemical device of claim 14 wherein said dissolved salt includes at least one electrolyte salt from the following group: $LiClO_4$, $LiBF_4$, $LiAsF_6$, $LiPF_6$, $LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, $LiC(CF_3SO_2)_3$, $LiN(SO_2C_2F_5)_2$, $LiPF_3(C_2F_5)_3$, $LiPF_3(CF_3)_3$, and $LiB(C_2O_4)_2$.

17. The electrochemical device of claim 14 wherein said dissolved salt comprises lithium bis(chelato)borate having five to seven membered rings.

18. The electrochemical device of claim 15 or 16 where said electrochemical device comprises a secondary battery.

19. The secondary battery of claim 17 further comprising a lithium metal oxide or lithium metal phosphate positive electrode, at least one porous separator, and at least one lithium-carbon, lithium-alloy, or lithium metal negative electrode.

20. The secondary battery of claim 17 wherein said dissolved salt comprises at least one lithium salt.

21. The secondary battery of claim 17 wherein said dissolved salt comprises $LiCF_3SO_3$.

22. The secondary battery of claim 17 wherein said dissolved salt comprises $Li(CF_3SO_2)_2N$.

23. The secondary battery of claim 17 wherein said dissolved salt comprises $LiC(CF_3SO_2)_3$.

24. The secondary battery of claim 17 wherein said dissolved salt comprises $LiN(SO_2C_2F_5)_2$.

25. The secondary battery of claim 17 wherein said dissolved salt comprises $LiPF_6$.

26. The secondary battery of claim 17 wherein said dissolved salt comprises LiAsF6.

27. The secondary battery of claim 17 wherein said dissolved salt comprises $LiBF_4$.

28. The secondary battery of claim 17 wherein said dissolved salt comprises $LiClO_4$.

29. The secondary battery of claim 17 wherein said dissolved salt comprises $LiPF_3(C_2F_5)_3$.

30. The secondary battery of claim 17 wherein said dissolved salt comprises $LiPF_3(CF_3)_3$.

31. The secondary battery of claim 17 wherein said dissolved salt comprises $LiB(C_2O_4)_2$.

32. The electrochemical device of claim 14 wherein said device is a capacitor.

33. The capacitor of claim 32 wherein said dissolved salt comprises at least one quaternary ammonium salt having an anion selected from the group consisting of: ClO_4^-, BF_4^-, AsF_6^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(CF_3SO_2)_3C^-$, $(C_2F_5SO_2)_2N^-$, $PF_3(C_2F_5)_3^-$, $PF_3(CF_3)_3^-$, and $B(C_2O_4)_2^-$.

34. A nonaqueous liquid type polymeric electrolyte having a main chain comprising Si and having an ionic conductivity of at least $6x10^{-4}$ S/cm at 25°C.

35. A nonaqueous liquid type polymeric electrolyte having an ionic conductivity of at least $8.4x10^{-4}$ S/cm at 37°C.

36. The nonaqueous liquid type polymeric electrolyte of claim 34 further characterized by having ionic conductivity of at least $8.4x10^{-4}$ S/cm at 37°C.

37. A lithium secondary battery containing the nonaqueous liquid type polymeric electrolyte of claim 34.

38. A capacitor containing the nonaqueous liquid type polymeric electrolyte of claim 34.

39. A lithium secondary battery containing the nonaqueous liquid type polymeric electrolyte of claim 35.

40. A capacitor containing the nonaqueous liquid type polymeric electrolyte of claim 35.

41. The nonaqueous liquid type polymeric electrolyte of claim 34 wherein said electrolyte is nonvolatile.

42. The nonaqueous liquid type polymeric electrolyte of claim 35 wherein said electrolyte is nonvolatile.

43. The nonaqueous liquid type polymeric electrolyte of claim 34 wherein said electrolyte is electrochemically stable over 4.5 V.

44. The nonaqueous liquid type polymeric electrolyte of claim 35 wherein said electrolyte is electrochemically stable over 4.5 V.

45. The nonaqueous liquid type polymeric electrolyte of claim 36 wherein said electrolyte is nonvolatile.

46. The nonaqueous liquid type polymeric electrolyte of claim 36 wherein said electrolyte is electrochemically stable over 4.5 V.

47. A capacitor containing a nonaqueous liquid type polymeric electrolyte having an ionic conductivity of at least 6×10^{-4} S/cm at 25°C.

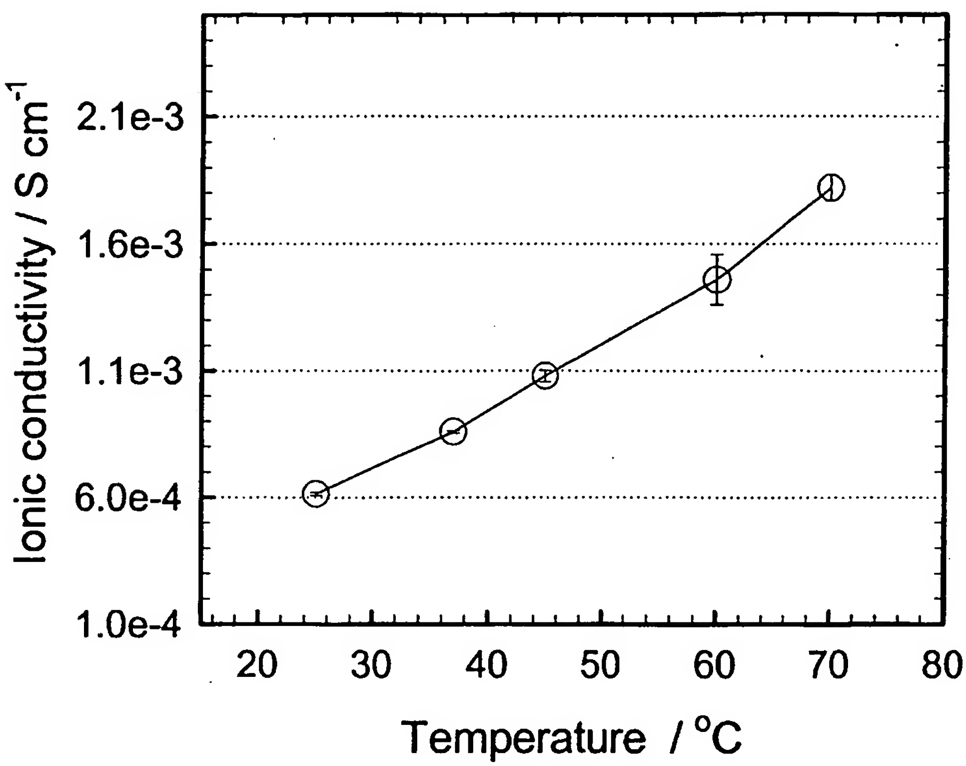

Ionic conductivity / S cm^{-1}
2.1e-3
1.6e-3
1.1e-3
6.0e-4
1.0e-4
20
30
40
50
60
70
80
Temperature / °C

FIGURE 1

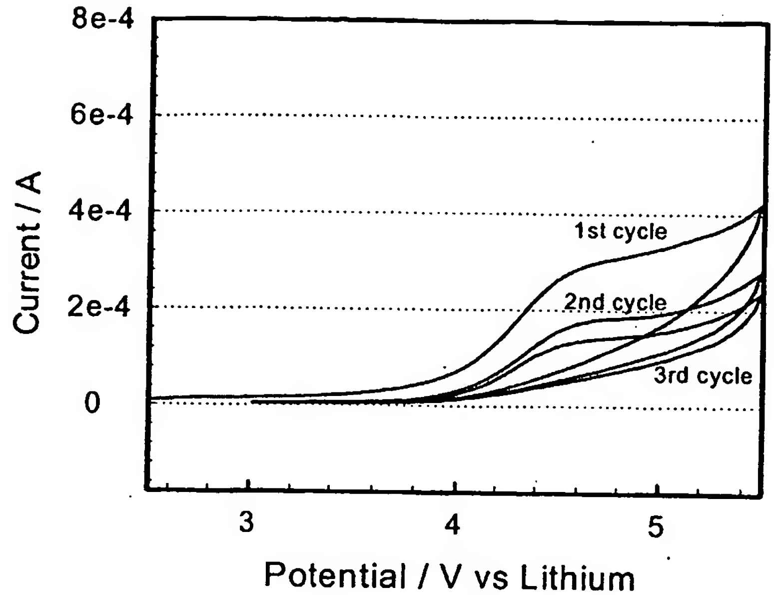


FIGURE 2a

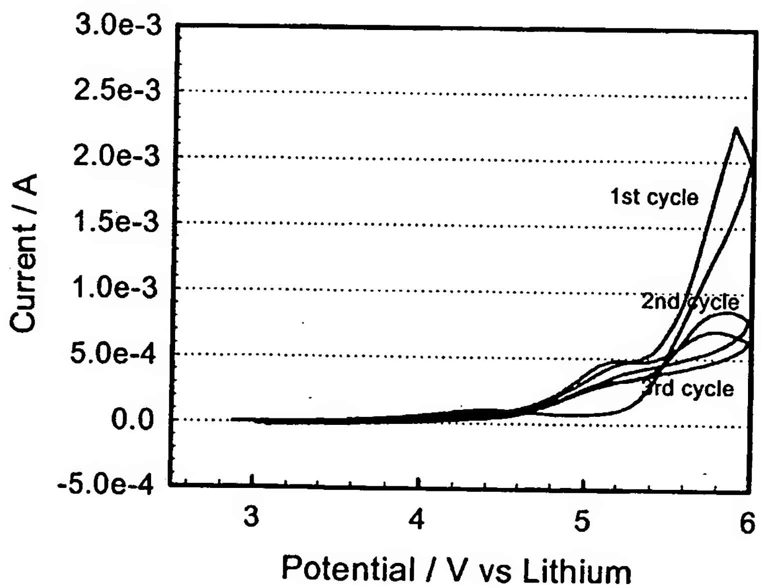


FIGURE 2b

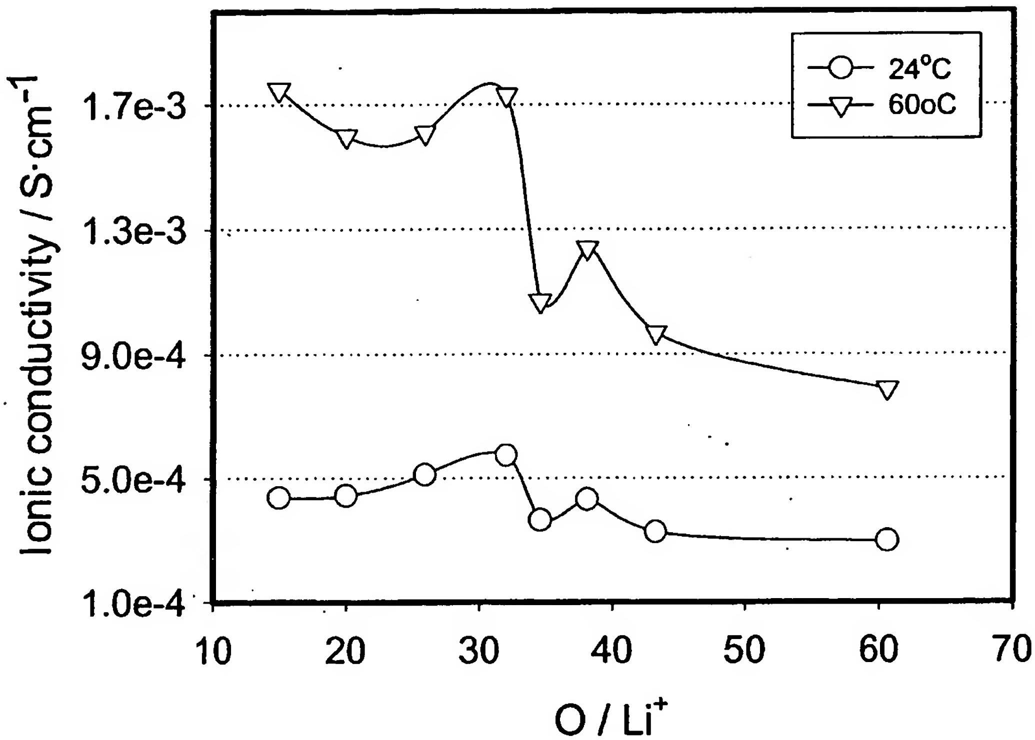

24°C
60oC
1.7e-3
1.3e-3
9.0e-4
5.0e-4
1.0e-4
Ionic conductivity / S·cm-1
10
20
30
40
50
60
70
O / Li+

FIGURE 3

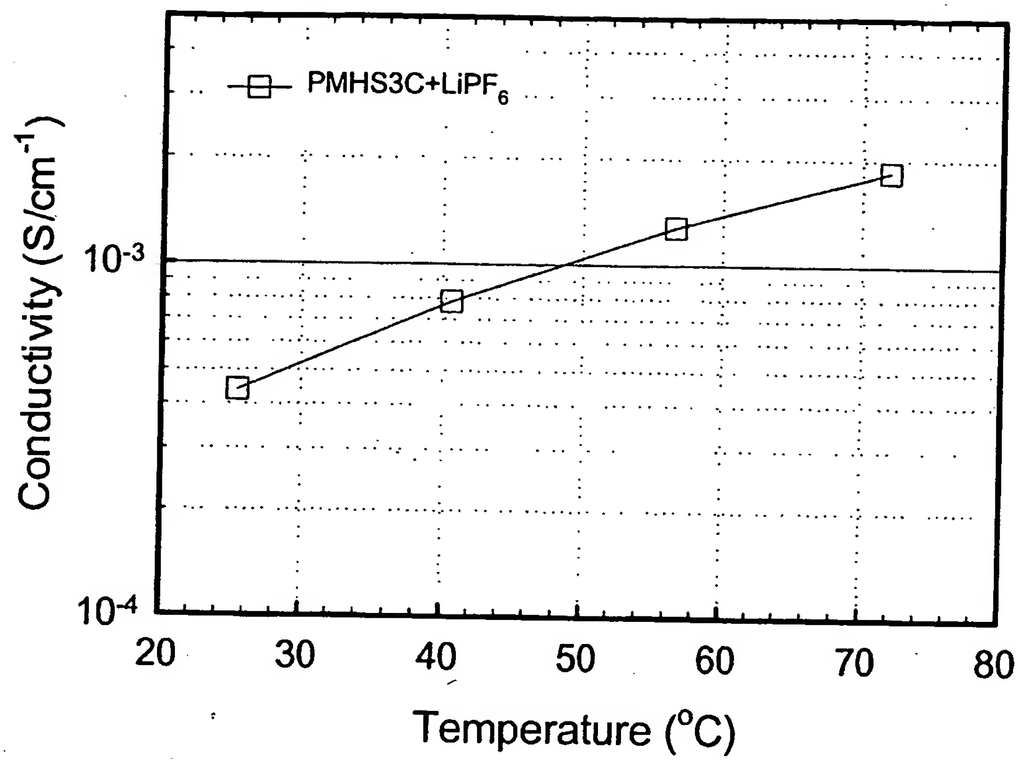
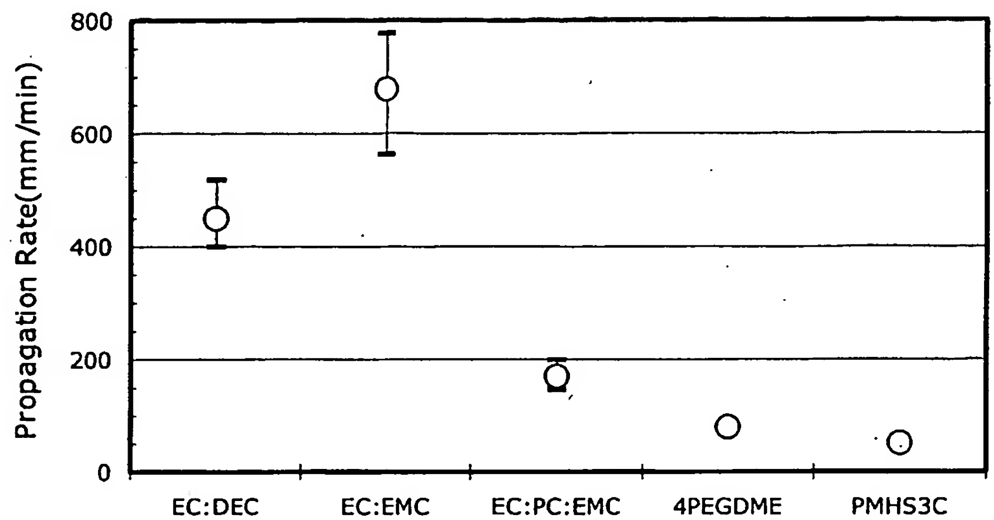

PMHS3C+LiPF6
Conductivity (S/cm-1)
10-3
10-4
20
30
40
50
60
70
80
Temperature (°C)

FIGURE 4



Propagation Rate(mm/min)
800
600
400
200
0
EC:DEC
EC:EMC
EC:PC:EMC
4PEGDME
PMHS3C

FIGURE 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/02127

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : H01M 6/14, 6/18, 10/40; H01G 9/025

US CL : 252/62.2; 429/188, 302-304, 313; 333, 321-323; 361/504, 505, 523

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/62.2; 429/188, 302-304, 313, 333, 321-323; 361/504, 505, 523

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,419,984 A (CHALONER-GILL et al) 30 May 1995 (30.05.1995), col. 4, lines 22-63 and col. 5, lines 18-col. 6, lines 53.	1,2,6,8,14,17-28 ---------- 3-5,10,13
X --- Y	US 5,885,733 A (OHSAWA et al) 23 March 1999 (23.03.1999), col. 2, lines 25-62 and col. 4, lines 19-67. See also claims 1-3.	1,6,8,14,17-28 ---------- 2-5,10,13
X --- Y	US 6,013,393 A (TANIUCHI et al) 11 January 2000 (11.01.2000), col. 1, lines 7-9; col. 1, lines 35-37; col. 4, lines 58-67.	34,37 ---------- 35,36,39,41,42
X --- Y	US 5,609,974 A (SUN) 11 March 1997 (11.03.1997), abstract; Table 1; col. 7, lines 47-55 and claims 1-3.	34,37,38 ---------- 35,36,39,40-46
A	US 5,112,512 A (NAKAMURA) 12 May 1992 (12.05.1992).	1-33

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 April 2003 (09.04.2003)	01 MAY 2003

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Pat Ryan Telephone No. 703-308-0661

INTERNATIONAL SEARCH REPORT

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,300,375 A (CHALONER-GILL) 05 April 1994 (05.04.1994).	1-33
A	US 5,362,493 A (SKOTHEIM et al) 08 November 1994 (08.11.1994).	1-33
A	US 5,538,812 A (LEE et al) 23 July 1996 (23.07.1996).	1-33
A	US 5,690,702 A (SKOTHEIM et al.) 25 November 1997 (25.11.1997).	1-33
A	US 6,124,062 A (HORIE et al.) 26 September 2000 (26.10.2000).	1-33

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/02127

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claim Nos.: 7,15 and 33
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Please See Continuation Sheet

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Please See Continuation Sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

Continuation of Box I Reason 2:
Claims 7, 15 and 33 were found to be unsearchable because they each recite "wherein said dissolved alkali metal salt comprises at least one quaternary ammonium salt having an anion...". However, an "ammonium salt having an anion" is not an "akali metal salt". Specifically, ammonium is not an alkali metal. It is unclear what Applicant intended to be encompassed by the subject claims and thus claims 7, 15 and 33 are unsearchable.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-33, drawn to a non-aqueous liquid polymeric electrolyte for an electrochemical device comprising poly(siloxane-g-ethylene oxide) and an alkali metal salt.

Group II, claim(s) 34-46, drawn to a nonaqueous polymeric electrolyte having an ionic conductivity of at least $6x10^{-4}$ S/cm at 25°C.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack unity of invention because they are not so linked as to form a single general inventive concept under PCT Rule 13.1.

In order for more than one species to be examined, the appropriate additional examination fees must be paid. The species are as follows:

1) A secondary battery; and,
2) A capacitor.

The claims are deemed to correspond to the species listed above in the following manner:

Claims 17-27, 29-31, 37 and 39 correspond to a secondary battery; and,
Claims 32, 33, 38 and 40 correspond to a capacitor.

The following claim(s) are generic: 1-16, 28, 34-36 and 41-46.

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: All of the groups are directed toward a non-aqueous liquid polymeric electrolyte, but each group has a special technical feature not shared by the remaining groups. Group I is directed toward a non-aqueous liquid polymeric electrolyte which has the special technical feature of a polysiloxane structure not shared by any of the remaining groups. Group II is directed toward a non-aqueous polymeric electrolyte which has the special technical feature of a specific ionic conductivity not shared by any of the remaining groups.

The species listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons: secondary batteries and capacitors are not analogous art.

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